

Heats of Formation and Isomerization of the Eight C_8H_{16} Alkylcyclohexanes in the Liquid and Gaseous States^{1,2}

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From experimental data recently obtained on the heats of combustion of the eight C_8H_{16} alkylcyclohexanes in the liquid state at 25° C, together with auxiliary data on the differences in the heats of vaporization at 25° C and on the difference in heat content of the gas between 0° K and 25° C, values are calculated for the following properties: the heat of isomerization of ethylcyclohexane into the given dimethylcyclohexane in the gas state at 25° C, and also in the gas state at 0° K; the heat of formation, from the elements, of the given isomer in both the liquid and gas states at 25° C and in the gas state at 0° K. The relation of the energy content to the structure of these molecules is discussed, including the labeling of the lower and higher-boiling forms of 1,3-dimethylcyclohexane as *cis* and *trans*, respectively.

I. Introduction

Values were recently reported for the heats of formation of the normal alkylcyclopentanes and normal alkylcyclohexanes [1].³ This report presents values of the heats of formation, for the gaseous and liquid states, and isomerization, for the gaseous state, of the eight C_8H_{16} alkylcyclohexanes, based on the results of measurements recently reported [2] on the heats of combustion of the eight C_8H_{16} alkylcyclohexanes in the liquid state at 25° C.

II. Results

The results of the present calculations are given in table 1. The values in column 2 are the results of the measurements of the heats of isomerization at 25° C in the liquid state [2]. These measurements were made in a manner similar to that previously reported for the eight C_9H_{12} alkylbenzenes at 25° C in the liquid state [3]. The values in column 3 are the differences in the heats of vaporization at 25° C, with the gas in the thermodynamic standard state of unit fugacity [4.]

The values in column 4 are the heats of isomerization at 25° C in the gaseous state, obtained by combining the values in columns 2 and 3. The values in columns 5 and 6 give the heats of formation, from the elements, solid carbon (graphite) and gaseous hydrogen, for the C_8H_{16} alkylcyclohexanes in the liquid and gaseous standard states, respectively. These values were obtained by combining the values previously reported for the heats of formation of gaseous and liquid ethylcyclohexane [1] with the values of the heats of isomerization given in columns 2 and 4.

Column 7 gives the differences of the values of the heat content at 298.16° K less that at 0° K for these compounds in the standard gaseous state [5]. The values in column 8 give the heats of isomerization at 0° K for the standard gaseous state, obtained by combining the values in columns 4 and 7. The values in column 9 give the heats of formation, from elements, solid carbon (graphite) and gaseous hydrogen, for the hydrocarbon in the standard gaseous state at 0° K. The value for the heat of formation of ethylcyclohexane in the standard gaseous state at 0° K was obtained from the corresponding value for 25° C, in column 6, and the values for the heat content at 298.16° K less that at 0° K for gaseous ethylcyclohexane [5], solid carbon (graphite) [6], and gaseous hydrogen [6].

¹ This investigation was performed at the National Bureau of Standards jointly by the Thermochemical Laboratory and the American Petroleum Institute Research Project 44.

² Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Atlantic City, N. J., April, 1947.

³ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1.—Values of the heats of isomerization and formation of the C₈H₁₆ alkylcyclohexanes

Compound	ΔH° (isomerization) for the liquid state at 25° C ^a	Difference in the heats of vaporization at 25° C ^d	ΔH° (isomerization) for the gaseous state at 25° C ^a	ΔH_f° (liquid) at 25° C ^f	ΔH_f° (gas) at 25° C ^g	Difference in ($H^\circ_{298.16} - H^\circ_0$) for the gaseous state ^b	ΔH° (isomerization) for the gaseous state at 0° K ^e	ΔH_f° (gas) at 0° K ^g
	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole	kcal/mole
Ethylcyclohexane	0.00	0.00	0.00	-50.72±0.37	-41.05±0.37	0.00	0.00	-28.94±0.38
1,1-Dimethylcyclohexane	-1.58±0.28	-0.63±0.04	-2.21±0.28	-52.30±0.46	-43.26±0.46	-0.22±0.01	-1.99±0.28	-30.93±.47
<i>cis</i> -1,2-Dimethylcyclohexane	-0.08±0.25	-.18±.01	-0.10±.25	-50.64±.45	-41.15±.45	-.09±0.01	-0.01±.25	-28.95±.46
<i>trans</i> -1,2-Dimethylcyclohexane	-1.46±0.27	-.51±.01	-1.97±.27	-52.18±.46	-43.02±.46	-.00±0.01	-1.97±.27	-30.91±.47
<i>cis</i> -1,3-Dimethylcyclohexane ^a	-2.57±0.22	-.54±.01	-3.11±.22	-53.29±.43	-44.16±.43	-.03±0.01	-3.08±.22	-32.02±.44
<i>trans</i> -1,3-Dimethylcyclohexane ^b	-0.85±0.21	-.30±.01	-1.15±.21	-51.57±.43	-42.20±.43	-.03±0.01	-1.12±.21	-30.06±.43
<i>cis</i> -1,4-Dimethylcyclohexane	-0.83±.21	-.34±.01	-1.17±.21	-51.55±.43	-42.22±.43	-.03±0.01	-1.14±.21	-30.08±.43
<i>trans</i> -1,4-Dimethylcyclohexane	-2.45±.22	-.62±.01	-3.07±.22	-53.17±.43	-44.12±.43	-.02±0.01	-3.05±.22	-31.99±.44

^a This isomer, formerly labeled "*trans*", has the following properties [7]: boiling point at 1 atm, 120.09°C; refractive index, n_D at 25° C, 1.4206; density at 25° C, 0.7620 g/ml.

^b This isomer, formerly labeled "*cis*", has the following properties [7]: boiling point at 1 atm, 124.45°C; refractive index, n_D at 25° C, 1.4284; density at 25° C, 0.7806 g/ml.

^c Heat of isomerization of ethylcyclohexane into each of the dimethylcyclohexanes, H° (dimethylcyclohexane, liquid) $-H^\circ$ (ethylcyclohexane, liquid) at 25° C.

^d The difference in the standard heats of vaporization, [H° (gas) $-H^\circ$ (liquid)] (dimethylcyclohexane) $-[H^\circ$ (gas) $-H^\circ$ (liquid)] (ethylcyclohexane) at 25° C.

^e Heat of isomerization of ethylcyclohexane into each of the dimethylcyclohexanes, H° (dimethylcyclohexane, gas) $-H^\circ$ (ethylcyclohexane, gas) at the temperature stated.

^f Heat of formation, for the reaction 8 C (solid, graphite) $+8H_2$ (gas) $=C_8H_{16}$ (liquid, alkylcyclohexane), with each reactant and product in its standard state at 25° C.

^g Heat of formation, for the reaction 8 C (solid, graphite) $+8H_2$ (gas) $=C_8H_{16}$ (gas, alkylcyclohexane), with each reactant and product in its standard state at the temperature stated.

^h [$H^\circ_{298.16} - H^\circ_0$] (gas, dimethylcyclohexane) $-[H^\circ_{298.16} - H^\circ_0]$ (gas ethylcyclohexane).

The remaining values were obtained by combining this with the values in column 8. In table 1, the lower-boiling isomer, formerly labeled *trans*, is labeled *cis*, and the higher-boiling isomer, formerly labeled *cis*, is labeled *trans* [7], following the reasoning originally presented by Pitzer and Beckett [8] and confirmed here by the values of the differences in energy content.

III. Discussion

Pitzer and Beckett [8] have summarized in detail the possible configurations of the substituted cyclohexanes, showing that at ordinary temperatures substantially all of the molecules are in the "chair" configuration of the cyclohexane nucleus. In the cyclohexane ring in this configuration, each carbon atom is staggered alternately above and below a plane through the ring of carbon atoms, with the results that six of the substituents to the ring (hydrogen atoms or methyl groups) are in an "equatorial" belt around the ring, while three substituents are north "polar" above the ring, and three are south "polar" below the ring. If the six carbon atoms in the ring are twisted simultaneously so that the staggering with respect to the plane through the ring of carbon atoms is reversed, the six substituents that were originally equatorial become polar (three north and three south), while those that were polar become equatorial. When one or more of the substituents on

different carbon atoms are different, the inversion produces tautomers, and Pitzer and Beckett [8] give in detail the number and description of such tautomers for the several dimethylcyclohexanes. For example, in the case of *trans*-1,4-dimethylcyclohexane, one tautomer has both methyl groups polar and the other has both methyl groups equatorial. The tautomer with the methyl groups polar will possess a considerable amount of steric or strain energy (estimated by Pitzer and Beckett [8] to be near 4 kcal/mole) over that of the tautomer with both methyl groups equatorial, and the population of the higher energy state will be very small at ordinary temperatures.

For consideration of the relation between energy content and molecular structure, the values of energy content for the gaseous state at 0° K are preferably used, because all of the molecules of a given isomer will then be in the tautomeric state of lower energy, as well as being in the ground states, for translational, rotational, and ordinary vibrational energy. In the case of the example cited above, *trans*-1,4-dimethylcyclohexane, all of the molecules will be in the more stable tautomeric state with both methyl groups equatorial.

The conclusions reached by Pitzer and Beckett [8] together with the results of the present calculations, are summarized in table 2. The extraordinary accord of the values in the last two columns is to be noted. The difference in energy due to a

change of methyl group from an equatorial to a polar position, which is 2a according to Pitzer's [9] theoretical calculations, is evaluated from the experimental data to be 1.94 ± 0.10 kcal/mole.

TABLE 2.—Dimethylcyclohexanes in their more stable tautomeric forms, in the gaseous state at 0°K

Isomer	Position of the two substituents in the more stable tautomeric form (e, equatorial; p, polar) [8]	Theoretical strain energy (referred to two equatorial groups on nonadjacent carbon atoms as zero) (from Pitzer and Beckett, [8]).	Experimental difference in energy content ^c (referred to two equatorial groups on nonadjacent carbon atoms as zero)
			kcal/mole
<i>cis</i> -1,2-Dimethylcyclohexane....	<i>e, p</i>	3a	3.04 ± 0.21
<i>trans</i> -1,2-Dimethylcyclohexane...	<i>e, e</i>	a	$1.08 \pm .23$
<i>cis</i> -1,3-Dimethylcyclohexane ^a ...	<i>e, e</i>	0	$-0.03 \pm .17$
<i>trans</i> -1,3-Dimethylcyclohexane ^b ...	<i>e, p</i>	2a	$1.93 \pm .15$
<i>cis</i> -1,4-Dimethylcyclohexane....	<i>e, p</i>	2a	$1.91 \pm .15$
<i>trans</i> -1,4-Dimethylcyclohexane...	<i>e, e</i>	0	0.00

^a Formerly labeled "*trans*," see footnote a of table 1.

^b Formerly labeled "*cis*," see footnote b of table 1.

^c Includes the calculated correction (column 7 of table 1) from 25° C to 0° K.

The above considerations on energy content follow the conclusions originally reached by Pitzer and Beckett [8] and require that, among the 1,3-dimethylcyclohexanes, the isomer having the lower energy content be the "*cis*" isomer and that having the higher energy content be the "*trans*" isomer. These designations require a reversal of

the previous labeling of these two isomers, so that the lower boiling isomer formerly labeled *trans*, is now labeled *cis*, and the higher-boiling isomer, formerly labeled *cis*, is now labeled *trans* [10].

IV. References

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